



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of

Stuart F. Gordon et al

A METHOD OF PROCESSING A
PHOTOGRAPHIC ELEMENT
CONTAINING ELECTRON TRANSFER
AGENT RELEASING COUPLERS

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I hereby certify that this correspondence is being deposited today with the United States postal Service as first class mail in an envelope addressed to the Commissioner for Patents, Box 1450, Alexandria, VA 22313-1450.

Mary Capperell

Name: Mary Capperell

Date: 8/19/03

Commissioner for Patents

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Sir:

DECLARATION UNDER 37 C.F.R. § 1.132

I, Robert Alexander Arcus, declare:

1. I received a BS degree in Chemistry from the State University of New York at Stony Brook in 1973 and a PhD in Inorganic Chemistry in 1979. I have been a member of the American Chemical Society since 1973.
2. I joined Lockheed Missiles and Space Company in 1979 and worked on composite materials and adhesives for aerospace structures. In 1982, I joined the Research Laboratories of Eastman Kodak Company as a research chemist. I am currently a research associate in the Kodak Research Laboratories. My research contributions at Kodak have lead to several products that are currently on the market. I have published journal papers and conference papers on inorganic polymers, photoresist processing, and photographic film processing.
3. I am one of the co-inventors of the above referenced Application.

4. In 1999, we synthesized one of the compounds described by Nakai et al in U.S. 5,830,627 and in early 2000 we examined the photographic response of the compound in an experimental multilayer film that we put through a rapid development process. In particular, we incorporated Compound 2 (column 25 of U.S. 5,830,627) in an experimental multiplayer film format patterned after a Kodak 200 ASA film. Below is a description of the experimental protocol utilized and the results obtained.

Experimental film coatings:

We produced three separate coatings for our tests, which included a check film without any Zn complex and two films with different levels of the Zn complex (Compound 2 of Nakai). The experimental coatings were designed by Dr. Sidney Bertucci of Kodak and coated in two separate events. Although the films are not identical to those utilized in the examples of the current Application, both films used the same image coupler chemistry and image modifier chemistry (i.e. inhibitors, masking couplers) in the cyan layer. There was no additional chemistry added to either set of films that would modify the contrast other than the various ETARC and Zn complexes of interest. The emulsion type for both films was AgBrI T-grains, though the details of the emulsion structure are different. Experience with the two emulsion types would indicate that if a difference in susceptibility to an ETA compound was to be found, that the emulsions used to test the Zn compounds would be more likely to exhibit a higher contrast.

Coating 01 No additions

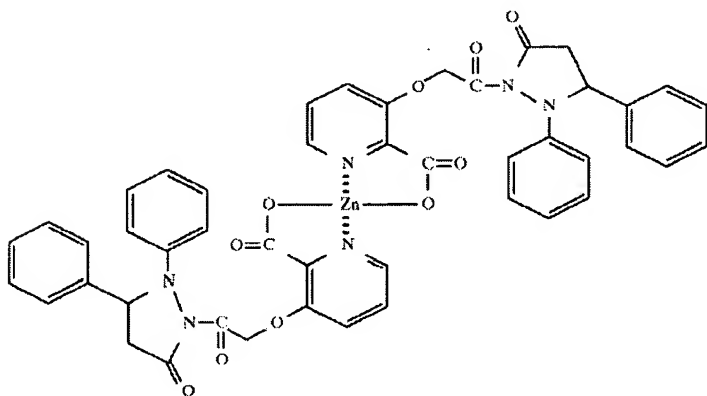
Coating 02 had 30 mg / sq ft of Zn complex added to both mid cyan and slow cyan layers

Coating 03 had 30 mg / sq ft of Zn complex added to the mid cyan later and 60 mg / sq ft added to the slow cyan layer.

The cyan color forming unit was coated as the first (bottom) light sensitive layer on an AHU layer on film base as in the examples in the current Application. Then the cyan layers were overcoated to produce a three color multilayer color negative film.

Zn complex:

The Zn complex (shown below) is Compound 2 that is listed in column 25 of U.S. 5,830,627 by Nakai.. It was added to the coating film melts as a dispersion that was 5% of the Zn complex and 7 % gel by weight. The synthesis of the below Zn complex was by Dr. Christopher Grote and the gel dispersion was made by Dr. Mary Christine Brick, both of Kodak.



Film exposure:

The exposure was for 1/25th of a second on a Kodak 1B sensitometer with a DL-V filter to simulate daylight exposure. The exposure was through a 21 step tablet that covered a density range from 0 to 4 density units in 0.2 density step increments. This allowed calculations of standard film parameters after processing.

Processing conditions:

The processing was done with 12" chops of film that were processed in 8 liters of each processing solution. Agitation of the developer solutions was by 2 second nitrogen burst every 6 seconds from the bottom of the tank. The bleach, fix, and wash solutions were agitated by constant stream of air bubbles. The temperature of the processing solution tanks was maintained by placing the tanks in a large constant temperature sink. The specifics of the processing time and temperature for each tank was as follows:

Solution	time (sec)	temperature
developer (listed below)	60	44.6 C
Kodak C-41RA bleach	45	40.6 C
Tap water wash	30	40.6 C
Kodak C-41 RA fixer	90	40.6 C
Tap water wash	30	40.6 C
Kodak photoflo rinse	60	40.6 C

The cross-over time was the last 5 seconds of each listed time above.

Developer compositions:

DEVELOPER FORMULATIONS in gms per liter		
developer	A	B
developer components	gm / liter	gm / liter
potassium sulfite	10	10
potassium bromide	2	2
hydroxyl amine sulfate	3	3
diethylene triamine pentaacetic acid, sodium salt	2.6	2.6
potassium carbonate	40.1	40.1
4-(N-Ethyl-N-2-hydroxyethyl)-2-methylphenylenediamine Sulfate	17.15	17.15
potassium iodide	0.004	0.004
poly(vinylpyrrolidone)K-15	3	3
2,6-pyridinedicarboxylic acid	0	8.4
water added to a volume of 1.0 liters		
pH (adjusted with KOH or H2SO4)	10.42	10.42

Results:

The following table lists the photographic responses for the three films in the two rapid developers, A and B, (the developers described in the table above).

result	Zn cmpd 2 in mg / sq ft	developer	MSC	OD
1	coating 1	none	A = NO PDA	--

2	coating 1	none	B = with PDA	6.90%	6.82%
3	coating 2	60	A = NO PDA	-5.79%	-4.34%
4	coating 2	60	B = with PDA	10.91%	9.71%
5	coating 3	90	A = NO PDA	-13.59%	-9.19%
6	coating 3	90	B = with PDA	10.69%	11.05%

MSC is Mid Scale Contrast, and for ease of analysis, we report the percent change in the contrast. OD is the over density and for ease of analysis, we report the percent change in the over density. PDA is 2,6-pyridine dicarboxylic acid and it is the additive for the rapid developer as described by Nakai.

We wish to highlight two observations from the above data table. Comparing result 1 with result 2 shows that the presence of 2,6-pyridine dicarboxylic acid can increase the contrast of a film that does NOT contain the Zn complex ETARC precursor of Nakai. Results 4 and 6 confirm the results of Nakai that the incorporation of the Zn complex can boost the contrast of the layer that it is coated in when the developer includes a tridentate ligand compound such as 2,6-pyridine dicarboxylic acid. However, comparing results 1, 3, and 5 show that the Zn complex is actually detrimental to the processing of the film when no 2,6-pyridine dicarboxylic acid is used. Incorporation of the Zn complex is deleterious to the processing of the film under such conditions. Since, as discussed above, the emulsions used to test the Zn compounds would be more likely to exhibit a higher contrast, the fact that the Zn compound is ineffective in this case is very strong evidence that it has no effect in these types of film structures without the tridentate ligand.

Conclusions:

The ballasted ETARC couplers of our invention provide a unique and effective way to amplify the signal in the film layer that they are incorporated in, especially in a rapid developer process. The method is independent of any additional developer component, such as the 2,6-pyridine dicarboxylic acid. This is particularly advantageous in

replenished developer systems where the concentration of the 2,6-pyridine dicarboxylic acid would be critical. In addition, we propose that the activity of the Zn complex might change as the developer seasons due the addition of other metal ions to the developer solution such as Ca that could compete for the 2,6-pyridine dicarboxylic acid ligand. The response of an ETARC precursor Zn complex that is dependent on the presence of a tridentate ligand such as 2,6-pyridine dicarboxylic acid to attain activity is NOT indicative of the response and activity of ballasted ETARC couplers of our invention.

5. I further declare that all statements made herein of my own knowledge are true and that the statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent resulting therefrom.

Date: August 15, 2003

Robert Alexander Arcus

Robert Alexander Arcus